Synthesis of Cu(II) aminoalkoxide complexes and their unusual thermolysis to Cu(0)

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Abstract

The "fluorine free" Cu(II) aminoalkoxide complexes $Cu(OCMe_2CH_2NR_2)_2$ (R = Me(I), Et(II)) are synthesized and characterized as a low melting solid (I) and a viscous liquid (II). The complexes are thermally decomposed at below 200 °C to produce metallic copper by unusual γ-hydrogen elimination reaction.
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Copper metal has attracted considerable interest as an interconnecting metal alternative to Al alloys for multilevel metallization applications in ULSI technology [1], due to its excellent electrical conductivity and good resistance to electromigration. The deposition of pure, conformal copper metal films is required for multilevel devices with <0.13 μm features. Therefore, the metal organic chemical vapor deposition (MOCVD) processes are increasingly important and have been extensively studied for copper thin films [2]. Copper thin films have been prepared by MOCVD using various precursors. In recent years, Lewis base-stabilized Cu(I) β-diketonate complexes such as (hfac)Cu(I)L (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate; $L = \eta^2$-alkynes [3], η^2-alkenes [4], dienes [5]), are used as copper CVD precursors to deposit pure copper films through a ther-

mally induced disproportionation reaction [6]. However, the thermal stability of these fluorinated β-diketonate adducts with Lewis bases are not satisfactory for the selective growth of copper films with reproducibility and copper thin films deposited are usually contaminated with carbon and fluorine without an external agent [7]. On the other hand, stable Cu(II) complexes have been employed as the precursors for copper thin films by MOCVD. A typical examples are MOCVD of $Cu(hfac)_2$ using H_2 as an external reducing agent [8] or Cu(β-diketonate)$_2$ and Cu(β-ketoiminate)$_2$ without an external reducing agent [9]. However, H_2 is crucial for the clean reduction of the precursor to the metal and lowering deposition temperature in this process [10].

Self-reducible Cu(II) alkoxide complexes are another candidates for copper MOCVD precursors. In this case, the intramolecular β-hydrogen/reductive elimination [11] or the intramolecular amine to imine conversion of the aminoalkoxide ligands mediated by the central Cu(II) ion [12] is the key step in production of copper metal. However, copper thin films deposited from these precursors are contaminated with carbon and fluorine.

In this communication, we report the synthesis of highly volatile copper complexes with donor-functionalized alkoxide ligands and their thermal properties in the absence of external reducing agents.

The novel bis(aminoalkoxide) Cu(II) complexes were synthesized from the alcohol exchange reaction [13] of Cu(II) methoxide with the corresponding aminoalcohols in toluene. The ligands of 1-dimethylamino-2-methyl-2-propanol(dmampH) and 1-diethylamino-2-methyl-2-propanol(deampH) were synthesized by the literature method with a minor modification [14]. After a typical work-up of the reaction mixture, target complexes could be obtained as a purple solid (I) and a viscous liquid (II). [2] Especially, **I** is a highly volatile solid and could be further purified by vacuum sublimation at temperatures of 30–40 °C at 10^{-2} Torr. Both **I** and **II** are highly soluble in organic solvents such as toluene or THF. The complexes are extremely moisture sensitive and the color of the complexes turned blue within a few minutes on exposure to air. IR spectra of the blue complexes showed broad absorption bands at 3500 and 1600 cm^{-1} due to OH vibrations of water molecules and the composition of these complexes was found to be $[Cu(L)_2]H_2O$ by elemental analyses of the complexes for C, H, and N. To identify the molecular structure of **I**, a single crystal X-ray diffraction study has been carried out. [3] Suitable single crystals for crystal structure determination were obtained by slow vacuum sublimation of **I**.

An ORTEP drawing of the molecule is shown in Fig. 1. Complex **I** shows a square planar structure in which the copper atom is located at the crystallographic inversion center. In the molecule, the copper center is coordinated by two oxygen atoms O(1), O(1A) and two nitrogen atoms N(1), N(1A) in a *trans* fashion. The Cu–O (1.863(1) Å) and Cu–N (2.058(1) Å) distances are comparable to those in similar molecules such as $Cu(OCHMeCH_2NMe_2)_2$ (Cu–O 1.856(3) Å, Cu–N 2.052(3) Å) [11b] and $Cu[OCH(CH_2NMe_2)_2]_2$ (Cu–O 1.851(4) Å, Cu–N 2.060(4) Å) [11b]. The bond angles O(1)–Cu–N(1) and O(1)–Cu–N(1A) are 86.41(8) and 93.59(8), respectively, which are close to the ideal 90° of a square plane.
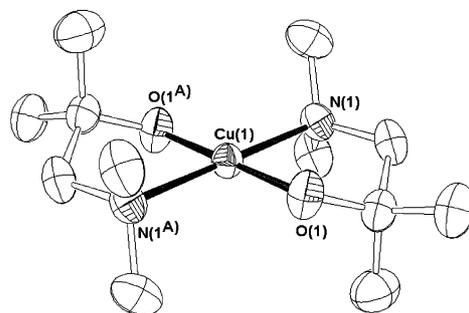

Fig. 1. Molecular structure of **I**, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) Cu(1)–O(1) 1.863(1), Cu(1)–N(1) 2.058(1), O(1)–Cu(1)–N(1A) 93.59(8), O(1)–Cu(1)–N(1) 86.41(8).

Thermogravimetric analyses for the complexes were conducted under an Ar atmosphere with a 10 °C/min temperature ramp and showed that **I** and **II** were sufficiently volatile (Fig. 2). Upon heating under an argon atmosphere, **I** and **II** undergo rapid weight loss in the temperature ranges of 100–200 and 60–170 °C, respectively. On the other hand, the DTA curves show exotherms around 200 °C which are presumably due to the decomposition of **I** and **II**.

The ligands dmamp and deamp have been employed for the synthesis of the volatile monomeric complexes. Indeed, our "fluorine-free" complexes are much volatile compared to other aminoalkoxide-containing copper complexes [11,12]. The major difference of the complexes from other Cu(II) aminoalkoxide complexes is two methyl groups attached to the C(α) position of the ligand. That is, two nonpolar methyl groups on the α-carbon effectively prevent oxygen and nitrogen atoms of the neighboring ligands from approaching the central copper atom to minimize intermolecular interaction. A direct thermal decomposition experiment for the complex **I** was carried out to investigate whether the complex can be used as a copper metal source. Thermolysis
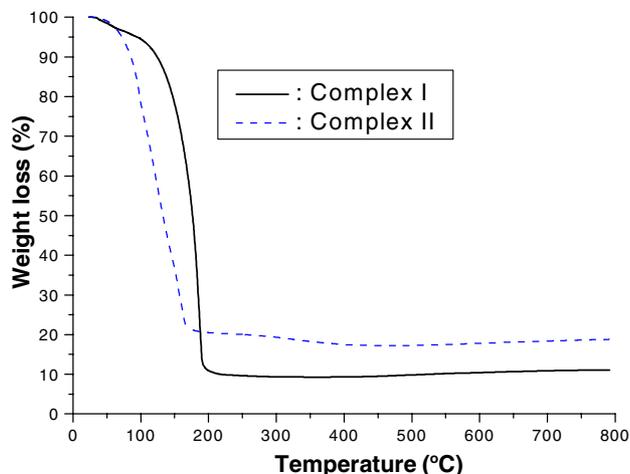
Fig. 2. TGA of **I** and **II** under Ar with a temperature ramp 10 °C/min.

of **I** under a nitrogen atmosphere (200 °C for 3 h) gave only the copper metal phase evidenced by X-ray powder diffraction (Fig. 3). XPS data of the powder also show that the most intense Cu LMM Auger transition peak and the Cu $2p_{3/2}$ photoelectron peak are observed at 918.5 and 932.8 eV, respectively, indicating that the resulting powder consists of only metallic copper. The GC/MS and ^{1}H NMR studies of by-products collected in a liquid N_2 trap during the thermolysis process revealed that **I** is thermally decomposed into HOC$(CH_3)_2CH_2$ N$(CH_3)_2$, $(CH_3)_2$ NCHCHN$(CH_3)_2$, acetone, and copper metal. The reduction pathway to produce metallic copper from **I** cannot be explained by β-hydrogen elimination and reductive elimination process as in the cases of Cu(OCH$_2$CH$_2$NMe$_2$)$_2$ and Cu(OCHMeCH$_2$NMe$_2$)$_2$ complexes [11], because there is no available β-hydrogen in **I**. Therefore, a possible mechanistic reduction pathway of **I** may be related with a C(α)–C(β) bond fission reaction as discussed in the recent report of Chi's group [12]. However, Chi's group reported that the thermolysis of Cu[OC(CF$_3$)$_2$CH$_2$N$(CH_3)_2$]$_2$ did not produce copper metal because it does not contain an amine proton, which is necessary for their mechanism.

We now propose the dialkylamino group assisted γ-hydrogen elimination reaction and a cooperative C(α)–C(β) bond fission reaction, followed by the reductive elimination reaction as shown in Scheme 1. Metallic copper was also obtained by the thermal decomposition of **II**. Moreover, the reaction of Cu(OMe)$_2$ with 1-diisopropylamino-2-methyl-2-propanol(dipampH) at 100 °C to prepare Cu(dipamp)$_2$ was not successful, producing metallic copper coated on the bottom of flask. It is suggested that more basic diisopropylamino group of the intermediate Cu(dipamp)$_2$ should lower the activation energy to decompose immediately via γ-hydrogen elimination pathway to produce copper film during the reaction.
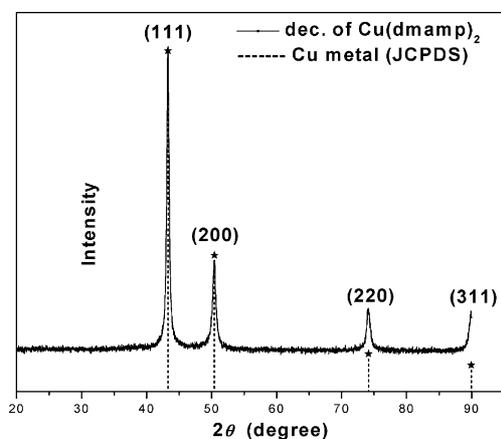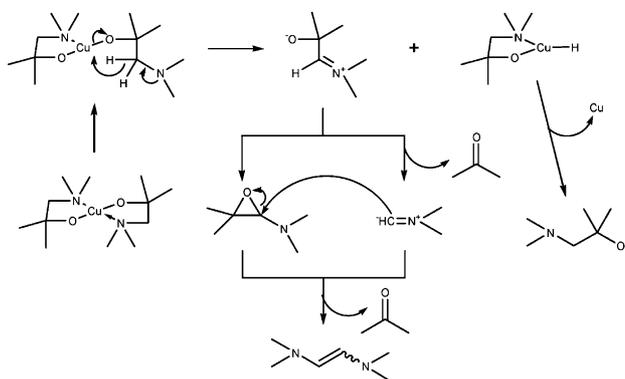

Scheme 1. Proposed mechanism of the thermal decomposition of Cu(OCMe$_2$CH$_2$NMe$_2$)$_2$.

Davis group's unclear explanation [11b] for the thermal decomposition study of Cu(OCH$_2$CH$_2$N $(CH_3)_2$)$_2$ by FT–IR could be explained clearly by our mechanism. Unclear C=N or C=C bond formation in decomposed products could be due to the formation of $(CH_3)_2$NCH=CHN$(CH_3)_2$, which could be formed from further reaction of unstable dimethylamino-carbanions.

In conclusion, we have synthesized the new Cu(II) aminoalkoxide complexes Cu(OCMe$_2$CH$_2$NR$_2$) (R = Me(I) and R = Et(II)), which could be thermally reduced to pure metallic copper without a reducing agent. The complexes **I** and **II** are decomposed to pure copper metal through the dialkylamino group assisted γ-hydrogen elimination reaction and a cooperative C(α)–C(β) bond fission reaction followed by the reductive elimination reaction at temperatures around 200 °C. Moreover, the high volatility and thermal stability of the complexes **I** and **II** are suitable for the deposition of copper thin films without a reactive carrier gas. Recently, we have successfully deposited pure copper thin films by MOCVD using the complexes **I** and **II** as single sources. In addition, we are preparing copper nanoparticles and copper/zinc oxide nanocomposites [15] via thermal decomposition.

Supplementary material available

X-ray structural determination, details of crystallographic data (CIF) and experimental section with spectroscopic data of IR, GC/MS, ^{1}H NMR, and XPS are available from the authors on request.

Acknowledgements

Fig. 3. X-ray diffraction pattern of copper powder obtained by thermolysis of **I** at 200 °C for 3 h.

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